"Challenges Involving Deposition of Counter-Electrode Systems in High Charge (> 100k CV/g) Ta Powders"

John Moore, Eric Zediak, Chris Coker, Abhijit Gurav

KEMET Electronics Corp.

Greenville, SC, 29606 USA

Abstract:

One of the biggest limitations to the use of high charge Ta powders, CV/g greater than 100,000, in making Ta capacitors is the ability to adequately provide a continuous, uniform, and highly conductive counter-electrode system. Whether that counter-electrode is made from MnO_2 or conductive polymer, the difficulty of getting these materials to penetrate and coat the very fine porosity and large surface area associated with these high charge powders is both physically and chemically pushing the limitations of present day technology. This article suggests methods for doing just that.

Along with these materials and process challenges themselves is the difficulty to verify the success of modifying these systems. There have been many advancements made in the science of Electron Microscopy that can provide tools to assist in these process and materials modification. High resolution SEMs, fine sectioning TEM analysis, and the use of FIB/STEM prove invaluable in reducing experiments and development time by providing more details of the chemical and physical state to the counter-electrode materials than traditional Wet -to-Solid capacitance loss measurement.

Physical and Chemical Challenges

The electronics industry continues to push the edge of its technology with new products each year. The trend for faster, smaller, with more features and less expensive has become more of a dogma than a clever marketing ploy. VCR's and Portable TV's are now so inexpensive that it's more economical to replace them than to get them fixed when they stop working. In the past 25 years, the Intel processor has gone from 2,500 transistors per chip to over 1.5 billion transistors. Fifty years ago there was one black, rotary, party line telephone per neighborhood. Today we have landline phones in every room, two and three lines to these phones, messaging and fax features and usually every person in the home over 13 years of age has their own cell phone as well. This technology can only be made affordable if components can be provided that are low in cost and provide performance needed in very small packages. To the Ta Capacitor World, this is termed CV/cc improvement, in which more capacitance is offered at a given voltage in a smaller volume. To understand the challenges involved with this, some of the basic manufacturing methods for making Ta capacitors must be explained.

To begin with, present day Ta capacitor technology start with pressing and sintering Ta powder into a pellet shape with a Ta wire inserted in this pellet to act as the anode part of the basis capacitor plate structure (See Fig 1).

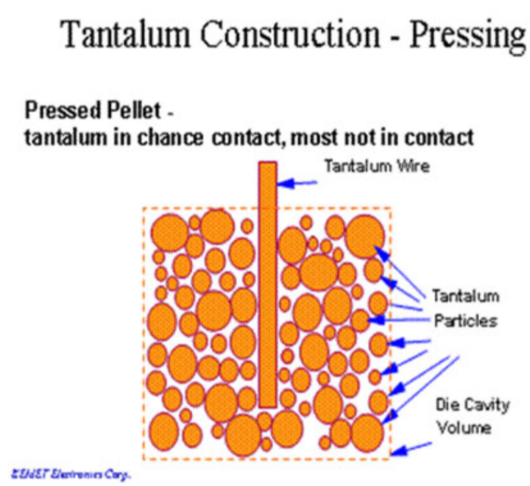

Fig 1

As the Ta powders used to make these pellets become finer, the surface area is increased increasing the available CV of the pellet, but the open pore structure associated with the pellet is decreased (See Fig 2).

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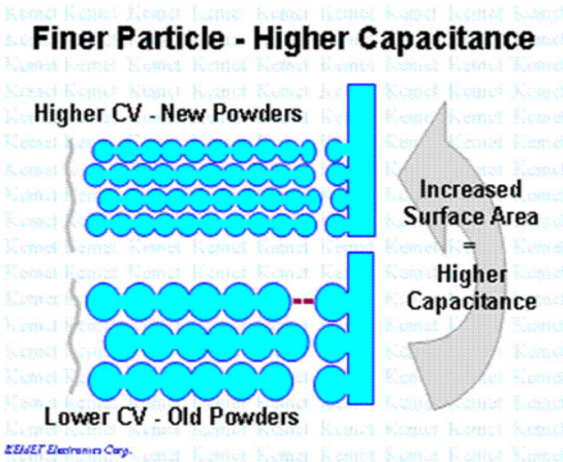


Fig 2

As the pore size decreases, it becomes more difficult to get the manganous nitrate solution to penetrate. There are two issues associated with this. First, the nitrate solutions themselves ere too viscous to penetrate the pores (Fig 3).

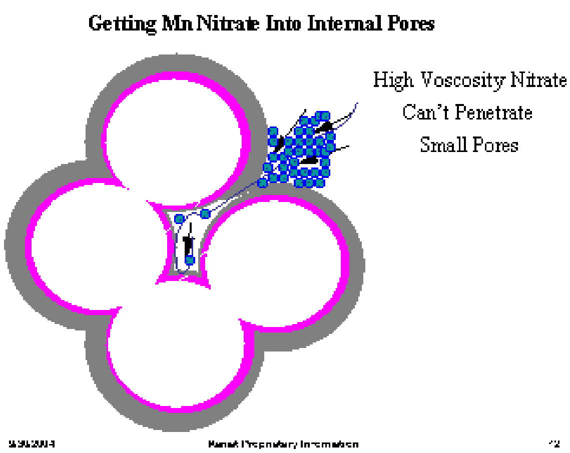


Fig 3

Second, even when the viscosity is lowered to allow penetration, there is difficulty with complete penetration believed to be due to entrapped air. This situation results in very thin internal coverage referred to as "black heart" (See Fig 4)

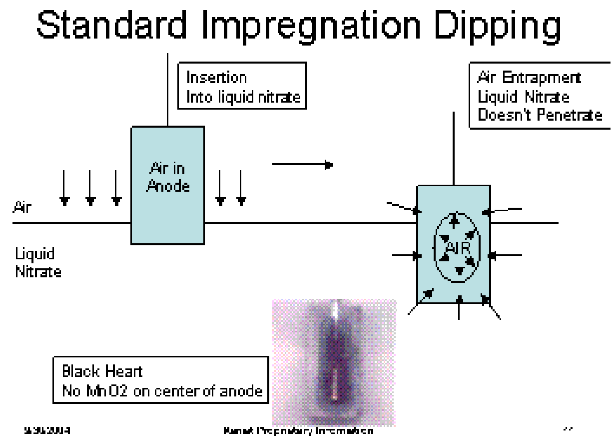
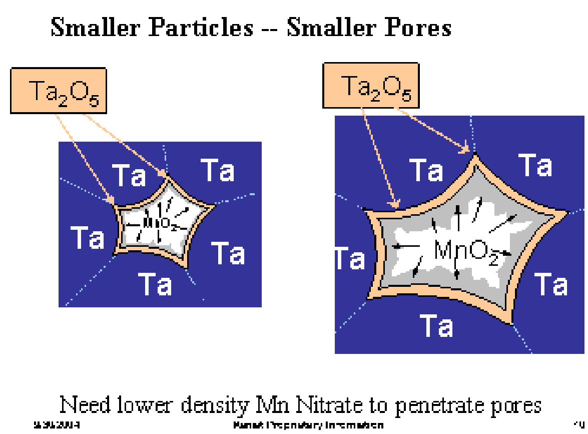


Fig 4

The use of lower viscosity (lower density) nitrate solutions also has limitations in that it requires more dip/conversion cycles to cover the surface. This is more costly than, and not as effective from a performance standpoint as, using higher density nitrate. As a result, the internal pore coverage with finer particle sized powders isn't as uniform, thick, or complete as more conventional sized Ta powders. This is visually demonstrated in the following schematic representation.



MnO2 Impregnation Modifications

A technology team was formed to investigate ways to modify the MnO_2 conversion process to improve the MnO_2 coverage of 150k CV/g Ta powder pellets. The following table lists many of the variables that can be changed to modify the process:

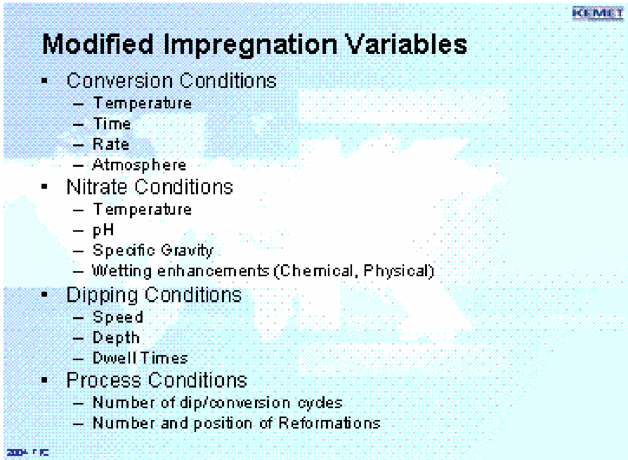
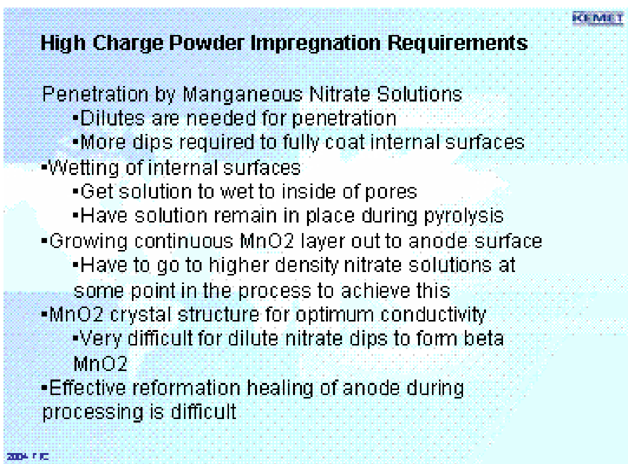


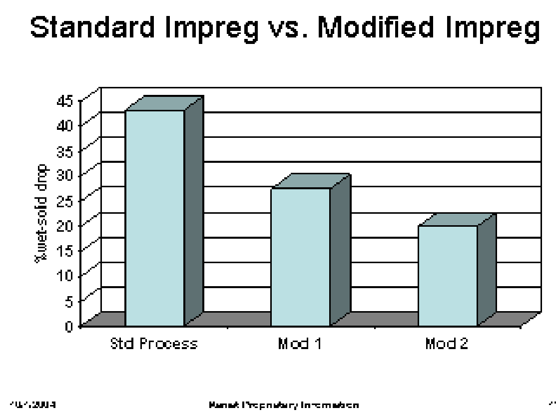
Fig 5

After analyzing these variables, there were some significant discoveries observed concerning high charge powders and their resultant Ta pellet pore structure.

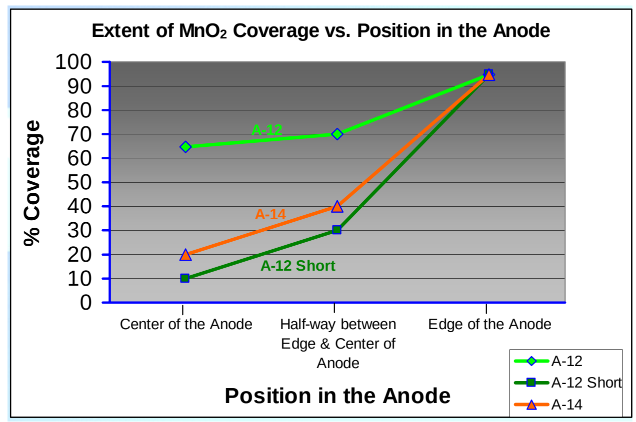


New Methods for Validation

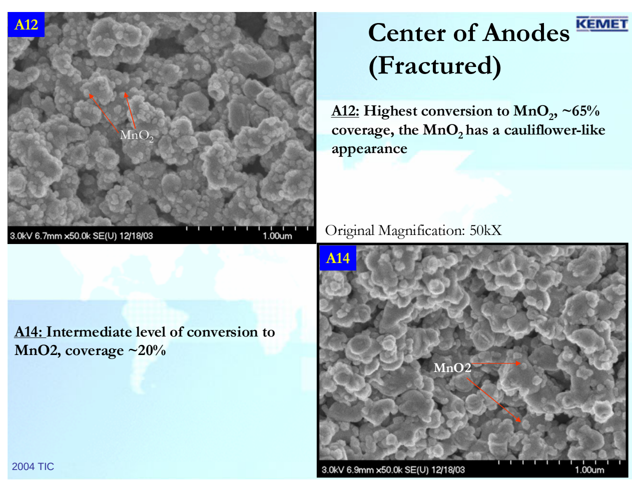
By doing various DOEs, working with the process and coming up with modifications that were theorized to work, the next step was to validate the new model. This was done by the old traditional method of Wet-to-Solid capacitance drop. The following chart indicates the success of the modified impregnation processes by the decreasing W-S drop.



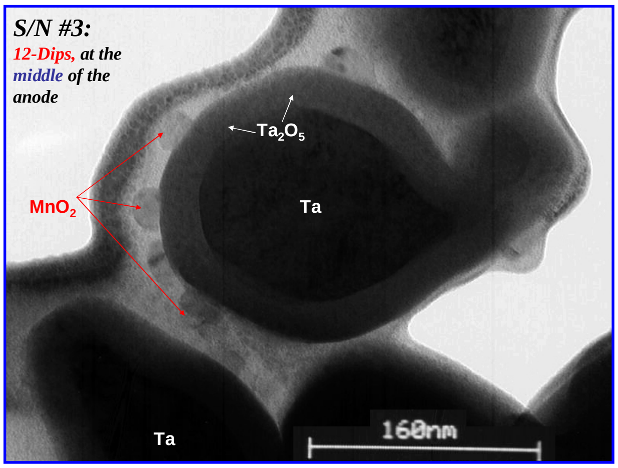
In addition to the W-S drop Scanning Electron Microscope analysis was use to make a quantitative measure of the amount of MnO_2 coverage in the center versus the edges of the pellet. In this way, a determination can be made as to how uniform the MnO_2 coverage is.



These coverage determinations were made with the aid of a new high resolution SEM. Some of the details can be seen below.



Through the use of a Transmission Electron Microscope (TEM) imaging the actual crystalline structure of the MnO2 and be determined. In addition to the standard TEM, one of the newest tools in the Electron Microscopy arsenal, the Focused ion Bean/Scanning Transition Electron Microscope allows the analyst to cut very fin cross-sections from the pellet, allowing the them to find areas of interest to observe, and then do high magnification (~800,000x) analysis of these areas. The FIB/STEM photo below actually shows MnO_2 Beta crystals growing on the Ta_2O_5 surface.



In this micro-photo, the large MnO_2 crystals that are observed were later determined to be beta phase. What is also present in this view, though not as obvious, is a thin MnO_2 layer covering the surface of the Ta particle that turned out to be polycrystalline MnO_2. From this photo, we determined that this modified process can cover the Ta surface and also produce the highly conductive beta phase. Knowing what was done in the process to produce both versions of MnO_2 can allow us to move in the direction of a more complete beta phase. We never would have seen this with traditional W-S capacitance measurements and solid test ESR measurements. These tests simply aren't sensitive or detailed enough to provide this type of information.

Conclusions

Although it involved major changes to the existing impregnation materials and processes, successful MnO_2 counter-electrode coverage of Ta pellets made from the highest CV/g powders can be achieved. Development time and cost can be reduced through the use of the latest tools in Electron Microscopy. These tools also help establish the best path forward to maximize the overall performance of the MnO_2 layer that is deposited.

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